



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C07C 45/28, 47/22, B01J 8/38, 23/31, 23/92, C07C 201/14</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/03809</b> <b>(43) International Publication Date:</b> 28 January 1999 (28.01.99)
<b>(21) International Application Number:</b> PCT/US98/14511 <b>(22) International Filing Date:</b> 14 July 1998 (14.07.98)  <b>(30) Priority Data:</b> 60/055,693 15 July 1997 (15.07.97) US  <b>(71) Applicants:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). ELF ATOCHEM, S.A. [FR/FR]; 10, La Défense, 4 & 8, cours Michelet, F-92800 Puteaux (FR).  <b>(72) Inventors:</b> CONTRACTOR, Rashmikan, Maganlal; 2302 Orchard Lane, Wilmington, DE 19810 (US). ANDERSON, Mark, William; 1224 Herold Circle, Charlottesville, VA 22901 (US). CAMPOS, Daniel; 5771 Pyles Fort Road, Wilmington, DE 19807 (US). HECQUET, Gérard; Résidence Foch, Appartement 32, 70, place Foch, F-62400 Béthune (FR). KOTWICA, Roland; la Porte-Moneau-Moru, F-60700 Pontpoint (FR). PHAM, Charlotte; 3, rue des Eglises, F-67700 Saverne (FR). SIMON, Michel; 8, rue Gustave Charpentier, F-57500 Saint Avold (FR).		<b>(74) Agent:</b> STEVENSON, Robert, W.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).  <b>(81) Designated States:</b> AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, HR, HU, ID, IL, IS, JP, KG, KP, KR, KZ, LC, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> IMPROVED VAPOR PHASE OXIDATION OF PROPYLENE TO ACRROLEIN		
<b>(57) Abstract</b> <p>An improved method for the selective vapor phase oxidation of propylene to acrolein in a recirculating solids reactor system using a bismuth molybdate multimetal oxide involving specific reactant concentrations (preferably 5 mol % to 30 mol % propylene, 0 to 20 mol % oxygen, and the remainder inert gas), particle size (1 to 300 micrometers), temperature (250 to 450 °C) and gas (1 to 15 seconds) and solids (2 to 60 seconds) residence times. Such a process leads to improved selectivity and propylene conversion.</p> <div data-bbox="922 1129 1380 1906" data-label="Diagram"> </div>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

TITLE OF THE INVENTION  
IMPROVED VAPOR PHASE OXIDATION  
OF PROPYLENE TO ACROLEIN

5

Technical Field

This invention relates to an improved vapor phase process for the catalytic oxidation of propylene to acrolein using as oxidant reducible particulate solids in an oxidized state, and where the resulting reduced solids are separately regenerated using molecular oxygen.

10

Background Art

An important route to acrolein is the vapor phase oxidation of propylene over a multicomponent catalyst containing molybdenum and/or other metals, usually as their oxides. The reaction step involves oxidation of propylene with air (oxygen) to form acrolein, along with carbon oxides, water and smaller amounts of other oxidized byproducts. Typically the reaction is carried out in multitubular fixed-bed reactors. The large exothermic heat of reaction and the thermal sensitivity of the propylene oxidation requires low feed concentrations, expensive heat transfer equipment, handling of a large volume of gas, and good reactor temperature control. Low propylene concentration is also required to avoid flammability conditions.

20

The magnitude of some of these problems is reduced when a fluidized-bed reactor is used. The temperature can be readily controlled within a few degrees because of the intensive solids mixing and the good heat transfer characteristics. Higher propylene concentrations can be used because the danger of flammability is reduced by introducing the propylene directly into the reactor rather than premixing it with air (oxygen). However, very high propylene concentrations and low oxygen-to-propylene ratios in the reactor may result in the over reduction of the solids and reduced selectivity to acrolein. Also, significant back-mixing of gases in the fluidized-bed reactor result in poorer contact between

25

- 2 -

gases in the bubbles and the solids, making it difficult to obtain high propylene conversion.

Modified forms of fluidized-bed reactor are known as recirculating solids reactor, transport bed reactor, transport line reactor, riser reactor, fluidization reactor, multi-chamber fluidized bed reactor, and by other names, depending on design and/or personal preference. In this application we will use the term "transport bed reactor" to mean any reactor in which solid particles are injected at one end of the reactor and carried along with gas reactants at high velocities and discharged at the other end of the reactor to a gas-solids separation vessel. A riser reactor, in which the reactor is a vertical pipe wherein the reactive solids and gases are fed in at the bottom, transported in essentially plug flow and removed at the top, is one example of a transport bed reactor. Another example is a pipeline reactor, in which the flow of solids and gases is other than vertically upwards. A transport bed reactor, as defined herein, includes a riser reactor or pipeline reactor which also incorporates a zone for fluidization; i. e., a zone where the gas velocities are sufficiently high to carry out a substantial portion of the solids fed, but with more back-mixing of solids than would occur in plug flow. We will use the term "recirculating solids reactor system" to mean a general reaction system with two reaction zones, in which two separate reactions take place, and which uses a particulate solid which circulates between the two reaction zones and takes part in both reactions. Optionally, either or both reaction zones may take place in a transport bed reactor or a fluidized bed. Such reaction systems have found use in catalytic cracking in petroleum refining and in other reactions.

U.S. Pat. No. 4,102,914 discloses a process for the preparation of acrylonitrile by passing a mixture comprising gaseous oxygen, propylene and ammonia, together with an ammoxidation catalyst, in a transport bed reactor while controlling the superficial linear gas velocity and solids feed rate at specific rates.

European Patent Office Publication No. 0 034 442 discloses a process for preparing unsaturated aldehydes by passing an unsaturated olefin and

an excess of gaseous oxygen into a transport bed reactor with a solid oxidation catalyst at a linear gas velocity of 1.5 to 7.5 meters/second to achieve substantially plug flow within the reactor. Reaction products are stripped from the catalyst with steam in the stripper chamber.

- 5 U.S. Pat. No. 4,668,802 discloses a process for preparing maleic anhydride by oxidizing butane using an oxidized vanadium-phosphorous oxide catalyst as oxidant rather than oxygen wherein the resulting reduced catalyst is separately regenerated, and the use of a recirculating solids reactor system for this reaction. Certain of the examples use a transport bed or riser reactor for the
- 10 butane oxidation reaction. Japanese Kokai 3-170,445 discloses a similar process for preparing acrolein and acrylic acid by oxidizing propane using an oxidized bismuth-molybdenum catalyst as oxidant.

- The concept of using propylene in a similar process to make acrolein was disclosed in a paper titled "Oxidation and Ammoxidation of Propylene over
- 15 Bismuth Molybdate Catalyst", J. L. Callahan et al, Ind. Eng. Chem. Prod. Res. Develop., Vol. 9, No. 2 (1970). The use of a bismuth molybdate composition as direct oxidant was tested, but under the conditions of their tests this process was judged unsatisfactory because of the large amount of solids requiring circulation. Instead a process of using the bismuth molybdate composition as oxidation
- 20 catalyst (rather than as direct oxidant) was chosen for commercialization. This paper does not disclose the improved reaction conditions of the present invention.

- U.S. Pat. No. 4,152,393 and 4,341,717 disclose a specific design of reactor which it is said could be used, among a variety of applications, for the oxidation of propylene to acrolein using an oxidized solids as oxidant and
- 25 regenerating the resulting reduced solids in its regeneration zone. A process example shows the ammoxidation of propylene using ammonia and an oxidized molybdenum-based catalyst as oxidant. The reactor consists of a single shell containing a reaction zone and a regeneration zone, using a specific design containing a first up-leg, a first down-leg, a second up-leg, a second down-leg and

- 4 -

a return leg such that fluidized solids may be transferred from one zone to the other by one route and back by a second route, and so that the gases from one zone are not transferred to the other zone. This reactor has a complicated design which offers numerous places for potential plugging and which limits the ability to  
5 independently monitor and control oxidation zone and reduction zone conditions. This patent does not disclose the improved reaction conditions of the present invention.

The concept of using an oxidized catalyst to oxidize propylene was also disclosed in a paper titled "Modeling of Propylene Oxidation in a Circulating  
10 Fluidized-bed Reactor", G. S. Patience et al., at a conference named "New Developments in Selective Oxidation II", and published by Elsevier Science B.V. (1994). However, while the theoretical model of this system demonstrated that it had potential use as an alternate reactor system for propylene oxidation, it listed numerous challenges and uncertainties for development of a working process.

15 U.S. Pat. No. 4,604,370 discloses a process for regenerating a spent molybdenum-bismuth based multi-oxide catalyst resulting from its use for the oxidation of propylene to acrolein by heating it in air to 380 to 500°C for at least 12 hours or to 500 to 540°C for at least 2 hours.

An advertising folder prepared by E. I. DuPont in 1973 titled  
20 "Chemical Technologies Worldwide" included a single sheet titled "Transport Bed Reactor Technology for Selective Processes", which described the general advantages of a transport bed or riser reactor, listing among typical applications the reaction of propylene to make acrylic acid and the reaction of propylene and ammonia to make acrylonitrile.

25 None of the above references disclose the necessary information to enable the economical use of a vapor phase process for the oxidation of propylene to acrolein using as oxidant particulate solids in an oxidized state, and where the resulting reduced solids are separately regenerated using molecular oxygen.

- 5 -

The preparation of multicomponent compositions containing molybdenum and/or other metals and their use as catalysts in the oxidation of propylene to make acrolein is well known in the art. For example, U.S. Pat. No. 4,677,084 and 4,769,477 disclose a process for making highly attrition resistant silica-based catalysts containing molybdenum, vanadium or other metals. The molybdenum catalyst composition described was stated to show good catalytic performance in a conventional process for making acrylonitrile from propylene and ammonia. Numerous other patents such as U.S. Pat. No. 3,631,099, GB 1,490,489 or JP 05,301,051 also disclose specific catalyst compositions containing molybdenum for use in the oxidation of propylene to acrolein in a fixed-bed or fluidized-bed process.

#### Disclosure of Invention

The present invention relates to an improved process for the selective vapor oxidation of propylene to acrolein in a recirculating solids reactor system using a bismuth molybdate multimetal oxide solids in oxidized form, the improvement comprising: (a) contacting a feed gas containing from 1 mol % to 100 mol % (preferably from 5 mol % to 30 mol %) propylene, 0 to 20 mol % oxygen, 0 to 70 mol % water, and the remainder inert gas with an effective amount of a bismuth molybdate multimetal oxide in oxidized form comprised of particles from 10 to 300 micrometers in size, in a transport bed reactor at a temperature of 250 to 450°C, a gas residence time in the reaction zone from 1 second to 15 seconds, and a solids residence time in the reaction zone from 2 seconds to 60 seconds; (b) removing the effluent produced in the transport bed reactor of step (a) and separating the resultant reduced solids from the effluent gases (preferably stripping off any effluent gases from the reduced solids), transporting the reduced solids to a regenerator zone of the recirculating solids reactor system, and recovering acrolein from the effluent gases; (c) oxidizing the reduced bismuth molybdate multimetal oxide in the regenerator zone using an oxygen-containing gas, at a temperature of 250 to 500°C at a solids residence time in the regenerator

zone of 0.5 minute to 10 minutes, and at an oxygen-containing gas residence time from 3 seconds to 30 seconds; and, (d) recycling the oxidized bismuth molybdate multimetal oxide produced in step (c) to the transport bed reactor.

It is an object of this invention to provide an improved vapor phase  
5 process using a transport bed reactor for the oxidation of propylene to acrolein using the oxidized form of an attrition resistant solid containing molybdenum, and where the resulting reduced solids are separately regenerated using gaseous oxygen.

#### Brief Description of Drawings

10 Figure 1 shows a schematic drawing of a recirculating solids reactor configuration in which the reaction zone is comprised of two parts, a fluid bed section and a riser section and the regeneration zone is comprised of a fluid bed section.

Figure 2 shows a schematic drawing of a recirculating solids reactor  
15 configuration in which the reaction zone is comprised of a riser section and the regeneration zone is comprised of two parts, a riser section and a fluid bed section.

#### Modes for Carrying Out Invention

The present invention relates to an improved process for the selective vapor oxidation of propylene to acrolein in a recirculating solids reactor  
20 system which includes a transport bed reactor and a solids regenerator. The transport bed reactor is preferably a riser reactor in which solid particles are injected at the bottom of a vertical pipe, carried upwards with gas reactants at high velocities and discharged to a gas-solids separation vessel, or a combination of a riser reactor with a fluidization zone. The reaction between gas and solids occurs  
25 in the riser pipe in a matter of seconds, as distinguished from a conventional fluidized bed reactor where the reaction time is a matter of minutes. Gas velocities in a riser reactor are about 2 to 15 times higher than in fluidized bed reactors; solids concentrations range from 2 up to about 40 times lower. The products of the above reaction are then sent to a conventional processing unit where the



- 7 -

desired acrolein is separated and recovered with any unreacted gasses being recycled for further processing.

The reduced solids are then re-oxidized in a separate oxidation step to enable their reuse for the oxidation of propylene. The reduced solids from the riser zone are first separated from the product gas, stripped of any carbonaceous species in a separate stripper zone and returned to the regenerator. This process permits independent control of the reactant gas concentrations, the gas residence time, and the solids residence time in each zone for optimum operation.

There are several advantages of the above reactive concept over the steady-state fixed bed or fluidized bed alternative. High selectivity is achieved because of plug flow and optimum oxidative state of the solids. Significant reductions are realized in product recovery costs because the regeneration off-gas stream is kept separate from the product gas stream, resulting in a highly concentrated product stream. High throughput rates are attributed to the independent control of variables for the two steps of the operation, resulting in reduced investment and decreased solids inventory.

When a hydrocarbon oxidation reaction is carried out in the absence of molecular oxygen, lattice oxygen from the surface layers of these mixed metal oxide solids gets consumed very rapidly, typically in a matter of seconds. When that occurs, the solids activity decreases dramatically. If the solid is allowed to remain in the reducing atmosphere, reduced surface layers are built up on an oxidized core because diffusion of the bulk lattice oxygen to the surface is generally very slow in most practical situations. These reduced layers decrease selectivity and cause excessive yield losses when they get oxidized in the solids regenerator to carbon oxides. Previous processes for the oxidation of propylene to acrolein processes which used an oxidant with a separate regeneration zone for the solids do not disclose the surprising benefit of a short residence time in the propylene oxidation/solids reduction zone.

In carrying out the inventive process, the feed gas to the propylene oxidation step contains about 1 mol % to 100 mol % propylene, preferably about 5 mol % to about 30 mol % propylene. Some of the propylene used in the feed may be provided by the unconverted propylene which is present in the recycled reaction gas. In some cases, propylene may be available as the predominant component in a mixture of gases including other hydrocarbons; for example, technical propylene used in industry may contain 95 mol % propylene and 0 to 5 mol % propane. As long as none of the other gases present significantly adversely affects the process, it may be more convenient to use this propylene-rich mixture in the feed gas as the source of propylene. The oxygen concentration in the feed gas can be from 0 to 20 mol %. Air can be used as the source of oxygen. The remainder of the feed can be any inert gas, such as nitrogen or recycled reaction gas containing mostly water, carbon monoxide and carbon dioxide, and possibly unconverted propylene.

The present invention uses an effective amount of a bismuth molybdate multimetal oxide in oxidized form. Preferably this is a specially hardened solid particle which resists attrition, such as disclosed in previously referenced U.S. Pat. No. 4,677,084 and 4,769,477. Numerous other bismuth molybdate metal oxide compositions are disclosed in the art for the vapor phase oxidation of propylene to acrolein, and are also suitable for the operation of this invention. It should be further appreciated that other transition metal oxidant systems known in the art to promote the oxidation of propylene to acrolein, such as for example but not by way of limitation the iron/antimony metal oxide solids, should be considered equivalent for purposes of the process of the present invention. The solid particles are preferably about 20 to about 300 micrometers in size.

The oxidation step is carried out in the reaction zone at a temperature of about 250 to about 450°C. The reactor gas exit pressure is typically 0-50 psig. The gas residence time in the reaction zone is about 1 second

- 9 -

to about 15 seconds, and the solids residence time in the reaction zone is about 2 seconds to 60 seconds. The upper limit of solids residence time will, of course, depend on the activity of the solids. If still active, the solids can be retained in the reaction zone for longer than 60 seconds. Preferably, the solids are removed from  
5 the oxidation step when the oxidative surface layer of the solids have been essentially reduced to a non-oxidized form. The solids in the reactor effluent are separated from the effluent gases, and the acrolein product is recovered from the effluent gases, both separations employing conventional techniques and equipment. The separated solids are referred to herein as the reduced solids  
10 because they are in a lower oxidation state than that of the fresh solids which enter the reaction zone. When appropriate to the embodiment, the reduced solids are preferably stripped of any reactor gases and then transported to the regeneration zone of the recirculating solids reactor system. The stripped reactor gases are mixed with the reactor effluent gases. Acrolein is recovered from the effluent  
15 gases of the reaction zone, and remaining gases may be vented or recycled to the reaction zone. Any off-gases from the regeneration zone can be vented after heat recovery. Since this reaction is highly exothermic, the heat removal from the recirculating reactor system can be done by use of cooling coils, preferably at the solids regenerator but if necessary also at the fluidization of feed and/or eventually  
20 at the riser.

The reduced solids are re-oxidized in the regeneration zone using an oxygen-containing gas such as air. The regeneration zone temperature is maintained at about 250 to about 500°C. The solids residence time in the regenerator zone is about 0.5 minute to, typically, about 10 minutes. The oxygen-  
25 containing gas residence time is about 3 seconds to about 30 seconds. Total gas flow rate and oxygen concentration must be sufficient to provide the needed oxygen for solids re-oxidation to occur within the selected gas and solids residence time. The oxidized solids are then recycled to the reaction zone.

The required amount of solids and the required solids circulation rate depend on the extent to which the solids oxidation reaction is carried out in the regeneration zone (as opposed to the reaction zone), the amount of propylene to be reacted, the amount of mobile (or reactive) oxygen contained by the solids, and the  
5 reaction zone process conditions that determine the amount of solids oxygen used per pass. When oxygen concentration in the reaction zone is low, or zero, and substantially all of the solids re-oxidation reaction is carried out in the regeneration zone, a high solids circulation rate is required. This rate may be reduced, to the extent that the solids re-oxidation reaction is carried out in the  
10 reaction zone.

A recirculating solids reactor system can be operated continuously to oxidize propylene without any gas-phase oxygen in the reaction zone. Such operation results in a higher selectivity to make acrolein than can be attained with conventional reactors, providing an adequate solids circulation rate is maintained  
15 to supply the needed oxidized solids. In order to minimize the gas phase oxygen in the reaction zone, gas phase oxygen is stripped from the oxidized solids before recycling them to the reaction zone.

Alternatively, if a recirculating solids reactor system is operated so as to oxidize propylene under conditions of temperature, oxygen and propylene  
20 partial pressures and residence time in the reaction zone identical to those used in conventional reactors, significantly higher conversion of propylene and significantly higher yield of acrolein are obtained.

The high selectivity to acrolein attained in the transport bed reactor is maintained even if the feed to the reaction zone has a very high propylene  
25 concentration. The gas feed can be 100% propylene.

Recirculating solids reactor systems can in general have many different reactor/regenerator configurations. For example, the reaction zone of the system can be comprised of a transport bed reactor, a fluidized bed reactor or other gas-solid reactors, as can the regeneration zone. The recirculating solids reactor

system employed in this invention utilizes a transport bed reactor for the reaction zone. Optionally the transport bed reactor may comprise a riser reactor, a pipeline reactor, or a riser or pipeline reactor combined with a fluidization zone. The regeneration zone of the regenerator can be comprised of a riser reactor, a pipeline reactor, a fluidized bed reactor of any type, or a combination of the above reactors. It is to be understood that the invention is not limited to the specific combination of reactors listed above.

A transport bed reactor is characterized by high gas velocities of from about 5 ft/sec (about 1.5 m/sec) to greater than 40 ft/sec (12 m/sec). At the lower end of the velocity range there can be a significant amount of local back-mixing of solids. Typically, the reactor line is vertically mounted with gas and solids flowing upward in essentially plug flow; i.e., a riser reactor. Preferably, the superficial gas velocity in the riser is maintained at 1 to 10 meters/sec. The flow can also be downward and the reactor line can be mounted other than vertically, i.e., a pipeline reactor.

The solids concentration in the reaction zone of the reactor can range from, typically, about 1 lb/ft<sup>3</sup> (16 kg/m<sup>3</sup>) to, typically, about 10 lb/ft<sup>3</sup> (160 kg/m<sup>3</sup>), depending on the gas velocity, particle size and density, and the solids circulation rate. Preferably, the solids flux (mass flow rate per unit area) is at 50 to 1000 kg/m<sup>2</sup>sec.

FIG. 1 is a schematic drawing of one of the recirculating solids reactor systems used in the examples. The reaction zone is comprised of a fluidization section 1 and a riser section 2. The feed gas enters 1 and the oxidation of propylene takes place in sections 1 and 2. The separator-stripper unit 3 separates and strips off the reaction zone effluent gases from the reduced solids. The acrolein product is recovered from the reactor effluent gases leaving 3. The reduced solids are transported to the regeneration zone which is comprised of the fluidized bed section 4. The reduced solids are re-oxidized in section 4 and the oxidized (regenerated) solids are then recycled to the fluidization section 1. The

alternate/additional feed line 5 can be used to feed additional oxygen to riser section 2. The recirculation solids reactor of this embodiment can also be operated with just the riser section 2 as the reaction zone. In this mode of operation the feed can be introduced into the riser section 2 through feed line 5.

5                   FIG. 2 is a schematic drawing of another recirculating solids reactor system used in the examples. The reaction zone is comprised of a riser section 11. The feed gas enters 11 and the oxidation of propylene takes place in 11. The separator-stripper unit 12 separates and strips off the reaction zone effluent gases from the reduced solids. The acrolein product is recovered from the reactor  
10 effluent gases leaving 12. The reduced solids are transported to the regeneration zone which is comprised of a riser section 13 and a fluidized bed section 14. The reduced solids are oxidized in this regeneration zone and the oxidized (regenerated) solids are then recycled to the riser section 11.

                  The reaction and regeneration zones can be within a single reactor,  
15 although better process control usually is achieved if the two are in separate units.

                  The conversion of propylene in percent is defined as 100 times the number of mols of propylene converted, divided by the number of mols of propylene in the feed. The selectivity to acrolein in percent is defined as 100 times the number of mols of propylene converted to acrolein divided by the total  
20 number of mols of propylene converted. The yield of acrolein in percent is defined as 100 times the number of mols of acrolein formed divided by the number of mols of propylene in the feed.

                  As indicated previously, there are a number of bismuth molybdate oxidants disclosed in the art as suitable for the oxidation of propylene to acrolein.  
25 the process of this invention is not limited to a particular method of making this solid, nor to a particular promoter.

                  The following examples are presented to more fully demonstrate and further illustrate various individual aspects and features of the present invention and the showings are intended to further illustrate the differences and advantages

- 13 -

of the present invention. As such the examples are felt to be non-limiting and are meant to illustrate the invention but are not meant to be unduly limiting.

#### Example 1

The attrition resistant solids used in the examples of this invention were prepared by substantially following the procedure in U.S. Pat. No. 4,677,084 and in particular the procedure found in Example 10. The starting solids used to make the attrition resistant solids were obtained following the procedure described in French patent application 97 0243 filed February 27, 1997 in the name of ELF ATOCHEM S.A. and in particular by using multicomponent molybdate obtained according to example 5 of the French patent application. The starting solids prepared according to this French application corresponds to the formula:  $\text{Mo}_{12}\text{Co}_{3.5}\text{Bi}_{1.1}\text{Fe}_{0.8}\text{W}_{0.5}\text{Si}_{1.4}\text{K}_{0.05}\text{O}_x$ . The procedure involved 60.9 grams of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  being dissolved in 20 mL of distilled water. Also, 20.2 grams of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were dissolved in 15 mL of distilled water and 31.2 grams of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were dissolved in 30 mL of distilled water acidified with 6 mL  $\text{HNO}_3$  at a concentration of 68% by volume. Separately 127.4 grams of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  were dissolved in 150 mL of water with heating and stirring then 7.4 grams of  $\text{WO}_3$  were added. The aqueous solution containing the cobalt was introduced dropwise over 20 minutes into the aqueous solution of the ammonium salts. The ferric solution was next introduced over 10 minutes and then the solution containing the bismuth over 15 minutes. A solution obtained by dissolving 0.2 grams of KOH and 12.8 grams of colloidal silica (at a concentration of 40 weight %) in 15 mL of water was added over 10 minutes to the resulting gel. The gel thus obtained was blended for 1 hour at ambient temperature and then 1 hour at 70°C. The gel was next dried for 18 hours at 130°C to obtain a solid precursor. The solid obtained was precalcined at about 225°C in air. This precalcined solid was then milled and mixed with polysilicic acid solution as described in Example 10 of the 4,677,084 patent. The slurry was then spray dried

- 14 -

and the resulting solids were calcined for 9 hours at about 450°C in air to produce the attrition resistant solids used in the following test 1 through 34 of Example 1.

A recirculating solids reactor system of the type shown in FIG. 1 was used to oxidize propylene to acrolein. The transport bed reactor consisted of a small fluidization section surmounted by a 5/8" diameter by 10' tall riser tube. The recirculating solids were transported up the riser tube with the reactant and product gases which are in plug flow. Reactant gas contact times were on the order of 1-5 seconds. Isothermal conditions were maintained by an electric furnace. Temperatures were maintained in the range of 250-450°C. Reactor pressure was maintained at atmospheric to 2 psig. Riser superficial gas velocity was in the range of 6.6-10.5 ft/sec. Riser gas contact time was in the range of 1.3 to 1.5 seconds. Propylene feed concentration was varied as shown in the tables which follow. Steam feed concentrations were in the range of 9-33 mol%. All feed flows were controlled by thermal mass flow controllers. Propylene and nitrogen were fed either to the fluidization zone or directly to the riser tube (by-passing the fluidization zone).

The solids and the product gas stream were separated in a stripper and a series of cyclones. The stripper was a 4' diameter fluidized bed. After disengagement and stripping from the solids, the product off-gas was fed to the product quench/absorption system. Solids contact time in the stripper was in the range of 15 seconds to 10 minutes. From the stripper, the solids were then transported to the regenerator.

The regenerator was a 4.5" diameter fluidized bed. Solids bed height (solids contact time) in the regenerator was controlled by differential pressure control between the stripper and regenerator. Air was fed to the regenerator to re-oxidize the solids. The solids contact time was in the range of 1-21 minutes. The off-gas from the regenerator off-gas was fed to the regenerator quench system after disengagement from the solids in a series of cyclones.



From the regenerator, the oxidized solids were then fed back to the fluidization section of the transport bed reactor. The solids circulation rate was in the range of 15-250 kg/hr.

5 The two off-gas quench systems for the product and regenerator off-gases were of identical design. A recirculating liquid served as a direct contact condenser/absorber for the products. Caustic was used on the product off-gas to absorb organic products and to dimerize the acrolein produced. Water was used on the regenerator off-gas.

10 A hot gas sample stream from the product off-gas was taken to two static water absorbers. The first was used to absorb  $C_2/C_3$  aldehydes and acids for quantitative analysis by an off-line gas chromatograph. The second was used as a pre-treatment absorber to remove aldehydes and acids which interfere with the analysis, prior to on-line gas chromatographic analysis of  $N_2$ ,  $O_2$ , propylene, CO and  $CO_2$ .

15 The regenerator off-gas was sampled down-stream of the water quench and analyzed for  $N_2$ ,  $O_2$ , propylene, CO and  $CO_2$ . Reactor performance was determined by on-line gas chromatograph analysis for non-absorbed components in each of the two off-gas streams. Water absorbed products were measured by off-line gas chromatograph analysis of the liquid sample absorber.

20 The composition of the feed gases are presented in the tables as mol % of propylene, steam and nitrogen. If air was employed the amount is identified in a footnote. In some of the tests the contact time may have been increased by directing the gasses to the bottom of the fluidized bed rather than the base of the riser (see FIG.1 feed line 5). The primary process variables in the  
25 tables below are abbreviated as follows: Fluid. Bed Temp °C (fluidized bed temperature in °C),  $C_3H_6$  Feed Conc. mol % (propylene feed concentration in mol percent), Gas Cont. Time sec (gas contact time in seconds), and Sol. Rate kg/hr (solids circulation rate in kilograms per hour). The primary responses were measured as key process variables were changed, and are abbreviated in the tables

- 16 -

below as follows: Propylene Conver. % (percent propylene conversion), and C<sub>3</sub>/C<sub>2</sub> Select. % (percent selectivity to C<sub>3</sub> and C<sub>2</sub> reaction products).

The tests were grouped into three sets (Tables 1, 2 and 3 below).

The first set (Table 1) included tests where all riser side feeds were to the  
5 fluidization bed.

Table 1

PROCESS VARIABLES					RESPONSES	
Test Num	Fluid. Bed	C <sub>3</sub> H <sub>6</sub> /steam /N <sub>2</sub> Feed Conc. mol %	Gas Cont Time sec	Sol. Circ. Rate kg/hr	Propylene Conver. %	C <sub>3</sub> /C <sub>2</sub> Select. %
10	1	351 10.5 /8.8 /80.6	2.0	25	22.5	85.0
	2	352 10.5 /8.9 /80.6	2.0	23	20.2	82.2
	3	359 11.1 /9.9 /79.0	2.3	131	46.4	85.1
15	4	355 11.6 /10.0 /78.4	2.4	252	61.3	83.7
	5	351 10.6 /9.3 /80.1	2.2	30	15.5	87.7
	6	352 10.5 /9.4 /80.1	2.1	78	26.2	82.9
	7	353 10.4 /9.3 /80.3	2.1	72	30.4	83.5
	8	350 10.6 /9.3 /80.1	2.2	72	27.2	82.5
20	9	351 10.6 /9.3 /80.1	2.3	72	24.9	83.5
	10	351 10.4 /9.1 /80.5	2.2	68	37.0	87.9
	11	352 14.7 /8.7 /76.6	2.0	58	27.1	89.3
	12	347 6.6 /9.2 /84.2	2.2	53	31.4	85.2
	13	350 9.6 /8.4 /82.0	2.0	40	26.9	88.0
25	14	350 10.5 /9.3 /80.2	2.2	135	57.0	84.3
	15	333 10.2 /8.8 /81.0	2.2	39	12.7	82.4
	16*	363 10.6 /8.7 /73.8	2.0	25	48.5	86.0
	17	373 10.6 /9.3 /80.1	2.1	23	17.9	81.4

\* 10 SCFH air feed to fluidization bed (6.8 mol % in feed).

The second set of tests (Table 2) included tests where the nitrogen feed was split between the fluidization bed and the riser to increase gas contact time and propylene concentration in the fluidization bed.

5

Table 2

PROCESS VARIABLES						RESPONSES	
Test Num	Fluid.	<u>C<sub>3</sub>H<sub>6</sub>/steam /N<sub>2</sub></u>	Gas	Sol.	Propylene	C <sub>3</sub> /C <sub>2</sub>	
	Bed	Feed	Cont.	Circ.	Conver.	Select.	
	Temp	Conc.	Time	Rate			
10	°C	mol %	sec	kg/hr	%	%	
	18 352	49.4/ 9.1 /41.5	3.9	17	7.9	40.3	
	19 345	26.9/ 9.1 /64.0	3.1	107	12.1	69.2	
	20 333	33.0/ 9.2 /57.8	2.6	95	23.9	89.8	
	21 328	49.1/ 9.1/ 41.8	3.9	13	4.5	32.5	
15	22 326	25.6/ 9.1/ 65.3	3.0	13	2.9	20.2	
	23 380	26.9/ 9.3/ 63.8	3.0	164	43.0	67.6	
	24 383	17.0/ 9.5/ 73.5	2.5	30	40.4	80.6	
	25 372	16.7/ 9.5/ 73.8	2.5	16	26.3	89.0	
	26 373	10.6/ 9.3/ 80.1	2.1	23	17.9	81.4	

The third set of tests (Table 3) included tests where all propylene feed was to the riser (no propylene in the fluidization bed).

5

Table 3

PROCESS VARIABLES						RESPONSES	
Test Num	Fluid.	<u>C<sub>3</sub>H<sub>6</sub>/steam /N<sub>2</sub></u>	Gas	Sol.	Propylene Conver.	C <sub>3</sub> /C <sub>2</sub> Select.	
	Bed	Feed	Cont.	Circ.			
	Temp	Conc.	Time	Rate			
10	°C	mol %	sec	kg/hr	%	%	
	27	350	21.1/ 9.5/ 69.3	1.5	18	21.3	92.3
	28	348	21.1/ 9.5/ 69.3	1.5	21	15.9	95.5
	29	347	24.0/ 9.6/ 66.3	1.5	22	15.7	94.6
	30	347	23.8/ 9.5/ 66.7	1.4	19	13.1	89.2
15	31	348	5.4/ 9.8/ 84.8	1.5	18	13.7	77.6
	32	345	21.1/ 9.5/ 69.4	1.4	17	17.8	91.5
	33	349	10.4/ 9.4/ 80.2	1.4	15	17.0	84.1
	34*	349	10.2/ 9.3/ 73.1	1.4	18	21.0	82.1

20

\* 10 SCFH air feed to fluidized bed (7.4 mol % in feed)

The results were very good with the best results obtained with propylene feed to the riser as in Table 3 (where there is plug flow and no back-mixing of gas). The best test results are as follows:

25

C<sub>3</sub>/C<sub>2</sub> Selectivity > 95 %  
 Riser+Fluid. Bed Conversion > 60 %  
 Solids Conversion Ratio < 400 kg/kg

- 19 -

Two tests (shown by \*) were run with air feed to the riser. One test was conducted with all feeds to the fluidized bed, and one with propylene feed to the riser. The fluidized bed feed test resulted in significantly higher riser conversion. The riser feed test resulted in somewhat higher conversion and little change to selectivity. The best performances were achieved when fully oxidized solids were reduced in the riser in such a manner that essentially all the readily labile oxygen is consumed and the solids are removed from the reducing atmosphere immediately.

### Example 2

In a manner similar to the procedure of Example 1, a series of four additional runs were performed in the recirculating solids reactor of the type shown in FIG. 1. In these runs propylene was converted to acrolein using commercially purchased bismuth molybdate multimetal oxide solids as the oxidant. The particular bismuth molybdate multimetal oxide solids employed had a history of being used commercially at DuPont's Beaumont facility for the manufacture of acrylonitrile and been rejuvenated after showing a decline in activity relative to the manufacture of acrylonitrile. The rejuvenation process involved addition of molybdenum to the spent catalyst. The process variables and test result data are presented in Table 4.

Table 4

PROCESS VARIABLES					RESPONSES	
Test Num	Fluid. Bed	$C_3H_6$ /steam/ $N_2$ Feed	Gas Cont.	Sol. Circ.	Propylene Conver.	Acrolein and Acrylic acid Select.
	Temp °C	Conc. mol %	Time sec	Rate kg/hr	%	%
35	346	2.0/ 5.0/ 93	2.4	84	75.69	100
36	346	6.0/ 5.0/ 89	2.4	83	52.89	99.09
37	353	10/ 5.0/ 85	2.4	72.7	34.33	98.45
38	352	20/ 5.0/ 75	2.4	61	14.55	96.25

- 20 -

## Example 3

In a manner analogous to the procedure of Example 1, a series of four additional runs were performed in the recirculating solids reactor of the type shown in FIG. 1. In these runs propylene was converted to acrolein using essentially the same bismuth molybdate multimetal oxide composition as was used in Example 1. The only difference was that the salt precursor after drying was not precalcined at 225°C in air but instead was directly milled to the desired particle size range and mixed with polysilicic acid solution. This slurry was then spray dried and the resulting solids were precalcined at 225°C in air and then calcined at 450°C for 9 hours in air to produce the attrition resistant solids. The process variables and test result data for these additional runs are presented in Table 5.

Table 5

PROCESS VARIABLES					RESPONSES	
Test	Fluid.	$C_3H_6$ /steam/ $N_2$	Gas	Sol.	Propylene	Acrolein and
15 Num	Bed	Feed	Cont.	Circ.	Conver.	& Acrylic acid
	Temp	Conc.	Time	Rate		select.
	°C	mol %	sec	kg/hr	%	%
39	353	2.0/ 5.0/ 93	2.4	62	67.66	93.44
40	348	6.0/ 5.0/ 89	2.4	75	51.69	90.90
20 41	349	10/ 5.0/ 85	2.4	59	42.22	88.52
42	350	20/ 5.0/ 75	2.4	71	21.03	86.84

Having thus described and exemplified the invention with a certain degree of particularity, it should be appreciated that the following claims are not to be so limited but are to be afforded a scope commensurate with the wording of each element of the claim and equivalents thereof.

- 21 -

## Claims

We claim:

1. An improved process for the selective vapor phase oxidation of propylene to acrolein in a recirculating solids reactor system using a bismuth molybdate multimetal oxide in oxidized form, the improvement comprising:
  - (a) contacting a feed gas containing from 1 mol % to 100 mol % propylene, 0 to 20 mol % oxygen, 0 to 70 mol % water, and the remainder inert gas with an effective amount of the bismuth molybdate multimetal oxide in oxidized form comprised of solid particles from 10 to 300 micrometers in size, in a transport bed reactor at a temperature of 250 to 450°C, a gas residence time in the reaction zone of 1 second to 15 seconds, and a solids residence time in the reaction zone of 2 seconds to 60 seconds;
  - (b) removing the effluent produced in the transport bed reactor of step (a) and separating the resultant reduced bismuth molybdate multimetal oxide from the effluent gases, transporting the reduced bismuth molybdate multimetal oxide to a regenerator zone of the recirculating solids reactor system, and recovering acrolein from the effluent gases;
  - (c) oxidizing the reduced bismuth molybdate multimetal oxide in the regenerator zone using an oxygen containing gas, at a temperature of 250 to 500°C at a solids residence time in the regenerator zone from 0.5 minute to 10 minutes, and at an oxygen-containing gas residence time from 3 seconds to 30 seconds; and
  - (d) recycling the oxidized bismuth molybdate multimetal oxide produced in step (c) to the transport bed reactor.
2. A process as claimed in claim 1 wherein the feed gas contains from 5 mol % to 30 mol % propylene.
3. A process as claimed in claim 1 wherein the transport bed reactor is a riser or pipeline reactor.

4. A process as claimed in claim 1 where superficial gas velocity in the riser is maintained at 1 to 10 meters/sec.
- 5 5. A process as claimed in claim 1 where the bismuth molybdate multimetal oxide flux (mass flow rate per unit area) is at 50 to 1000 kg/sq. meter/sec.
6. A process as claimed in claim 1 where the regenerator zone is a fluidized bed, and the oxygen-containing gas to the regenerator is air.
- 10 7. A process as claimed in claim 1 where the bismuth molybdate multimetal oxide was prepared from a multimetal salt slurry by drying the slurry to produce a solid, precalcining the solid at a temperature of about 225°C, milling the precalcined solid to produce particles, adding the solid particles to a polysilicic acid solution, 15 spray drying and calcining the spray dried particles at about 450°C.
8. A process as claimed in claim 1 where the bismuth molybdate multimetal oxide is a commercial grade acrylonitrile catalyst.
- 20 9. A process as claimed in claim 1 where the bismuth molybdate multimetal oxide was prepared from a multimetal salt slurry by drying the slurry to produce a solid, milling this solid to produce particles, adding the solid particles to a polysilicic acid solution, spray drying, precalcining and calcining in air.



1/1

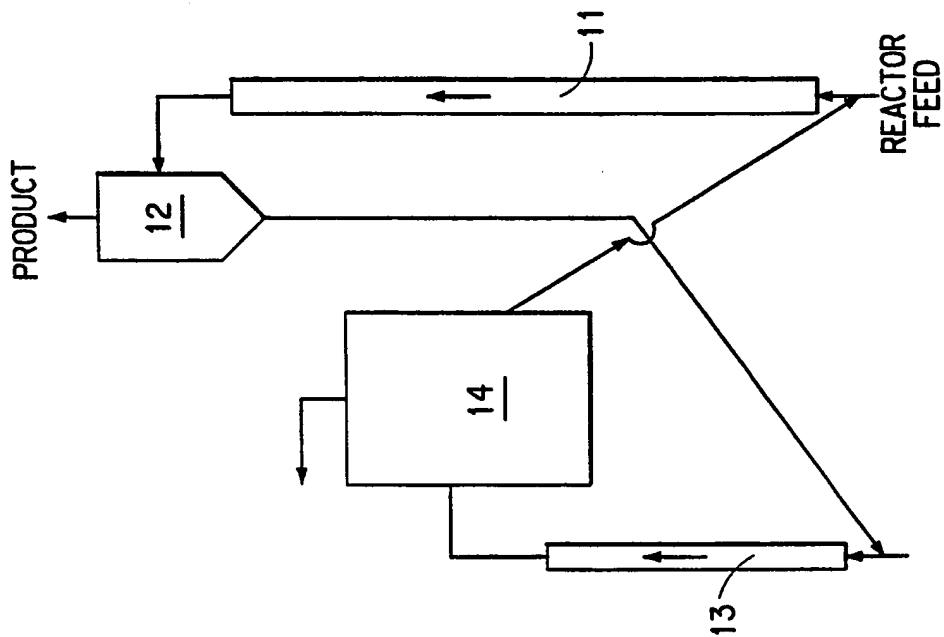


FIG. 2

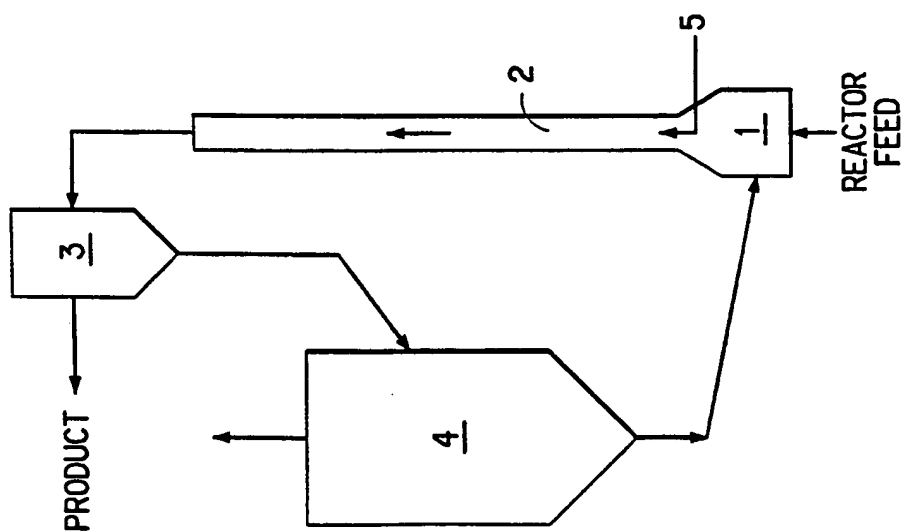


FIG. 1

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 98/14511

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C45/28 C07C47/22 B01J8/38 B01J23/31 B01J23/92  
C07C120/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 44 36 385 A (BASF AG) 18 April 1996 see the whole document --- -/--	1-9



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

5 October 1998

Date of mailing of the international search report

15/10/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3018

Authorized officer

Bonnevalle, E

## INTERNATIONAL SEARCH REPORT

Intern. al Application No

PCT/US 98/14511

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEMICAL ABSTRACTS, vol. 123, no. 14, 2 October 1995 Columbus, Ohio, US; abstract no. 173390, PATIENCE G S ET AL: "Modeling of propylene oxidation in a circulating fluidized-bed reactor" XP002079532 cited in the application see abstract & STUD. SURF. SCI. CATAL. (SSCTDM,01672991);94; VOL.82 (NEW DEVELOPMENTS IN SELECTIVE OXIDATION II); PP.1-18, DuPont Company;Experimental Station; Wilmington; 19880-0262; DE; USA (US) ---	1-9
Y	EP 0 034 442 A (STANDARD OIL CO OHIO) 26 August 1981 cited in the application see the whole document ---	1-9
Y	US 4 341 717 A (CALLAHAN JAMES L ET AL) 27 July 1982 cited in the application see the whole document ---	1-9
Y	EP 0 169 449 A (MITSUBISHI PETROCHEMICAL CO) 29 January 1986 cited in the application see claims ---	1-9
Y	US 4 659 689 A (SURESH DEV D ET AL) 21 April 1987 see the whole document -----	1-9

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/US 98/14511

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4436385 A	18-04-1996	US 5780700 A	14-07-1998
		BE 1008832 A	06-08-1996
		FR 2725715 A	19-04-1996
		IT M1952022 A	12-04-1996
		JP 8176019 A	09-07-1996
		NL 1001349 C	12-09-1997
		NL 1001349 A	12-04-1996
EP 0034442 A	26-08-1981	JP 56113726 A	07-09-1981
US 4341717 A	27-07-1982	US 4152393 A	01-05-1979
EP 0169449 A	29-01-1986	JP 1822148 C	10-02-1994
		JP 5029502 B	30-04-1993
		JP 61033234 A	17-02-1986
		US 4604370 A	05-08-1986
US 4659689 A	21-04-1987	NONE	